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# Electrical properties of methane hydrate + sediment mixtures

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Fire in the Ice

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## **Electrical properties of methane hydrate + sediment mixtures**

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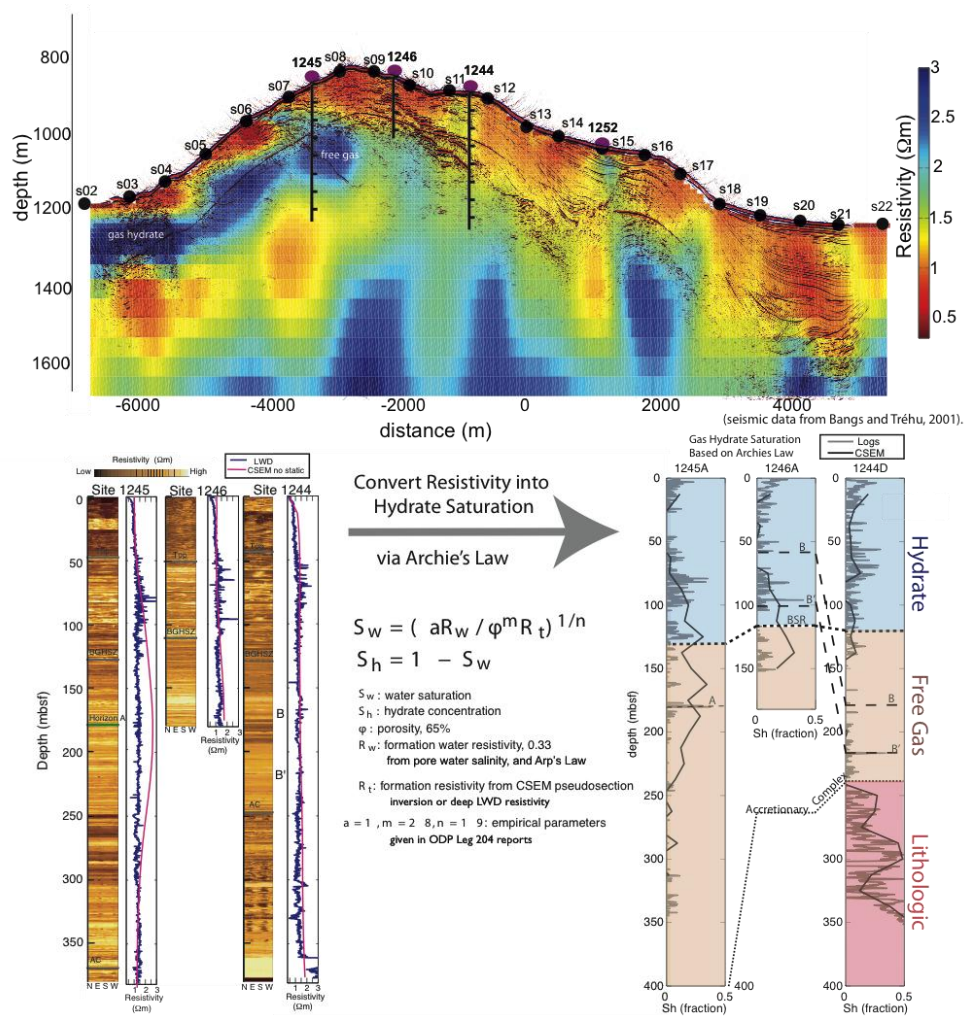
As part of our DOE-funded proposal to characterize gas hydrate in the Gulf of Mexico using marine electromagnetic methods, we established collaboration between SIO, LLNL, and USGS with the goal of measuring the electrical properties of lab-formed methane (CH<sub>4</sub>) hydrate and sediment mixtures. We examined samples with known characteristics in order to help relate electrical properties measured in the field to specific gas hydrate concentration and distribution patterns. Here we discuss first-ever electrical conductivity ( $\sigma$ ) measurements on unmixed CH<sub>4</sub> hydrate (Du Frane et al., 2011). The conductivity of CH<sub>4</sub> hydrate is  $6 \times 10^{-5}$  S/m at 5 °C, which is ~5 orders of magnitude lower than seawater. This difference allows electromagnetic (EM) techniques to distinguish resistive gas hydrate deposits from conductive water saturated sediments in EM field surveys. More recently, we performed measurements on CH<sub>4</sub> hydrate mixed with sediment and we also discuss those initial findings here. These results are important for predicting conductivity of sediments with pores highly saturated with gas hydrate. Furthermore, results on samples free of liquid water are an essential starting point for comprehensive mixing models.

## **Background**

Seismic methods have traditionally been used to map the spatial distributions of gas hydrates deposits. A bottom simulating reflector (BSR) indicates the lower limit of the stability field, typically marking the gas hydrate to free gas boundary, but provides little information about the occurrence of gas hydrate above it. Seismic blanking zones indicate hydrate or gas only at shallow depths near the seafloor. Besides acoustic properties, electrical properties can also be used to detect gas hydrate, because its high electrical resistance provides a suitable target for marine controlled source electromagnetic (CSEM) surveys.

CSEM sounding measures the amplitude and phase of EM energy through the seafloor at one or more frequencies; this data can be inverted to resistivity (see Figure 1). Pilot CSEM studies at Hydrate Ridge (2004) and the Gulf of Mexico (2008) indicate that CSEM is highly sensitive to concentration and geometric distribution of gas hydrate; however to make quantitative estimates of hydrate volume requires knowledge of the conductivity of gas hydrates in combination with petrophysical mixing relations established from theory and experiment. There have been few studies on the electrical properties of sediment/gas hydrate/water mixtures. Liquid water bearing samples help to resolve mixing laws, but lack characterization and are dominated by water with no

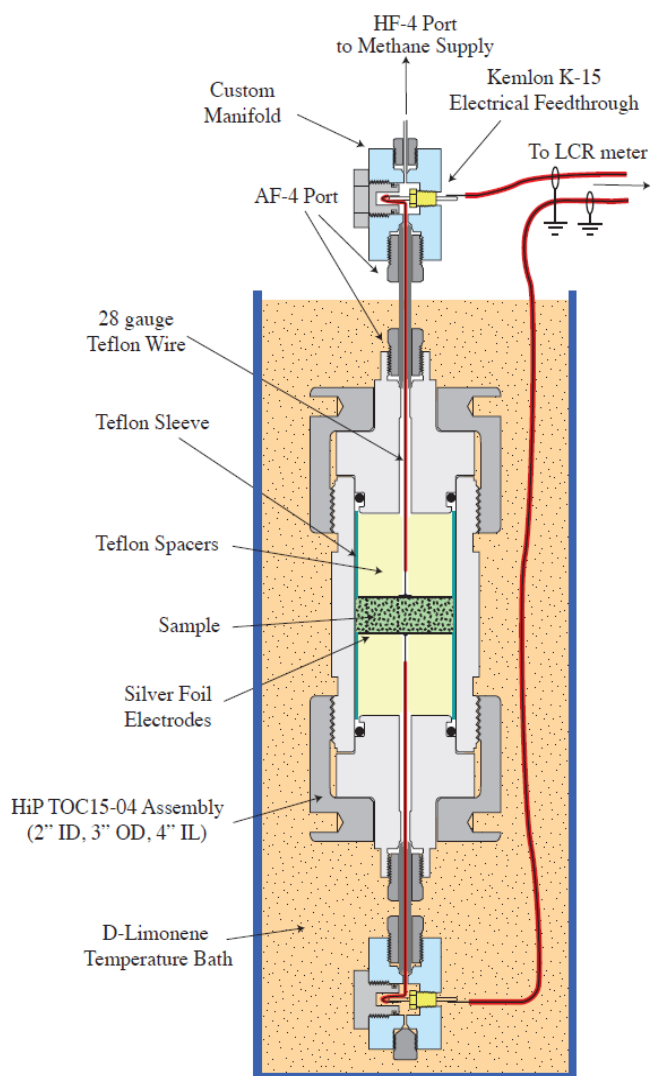
quantitative information on the conductivity of gas hydrate phase. It is well known that gas hydrates are resistive, but exactly how resistive are they?



**Figure 1.** Comparisons of inverted CSEM resistivity data to well log and seismic data at Hydrate Ridge showing the potential of CSEM as a complementary geophysical method for gas hydrate assessment.

## Making Gas Hydrate

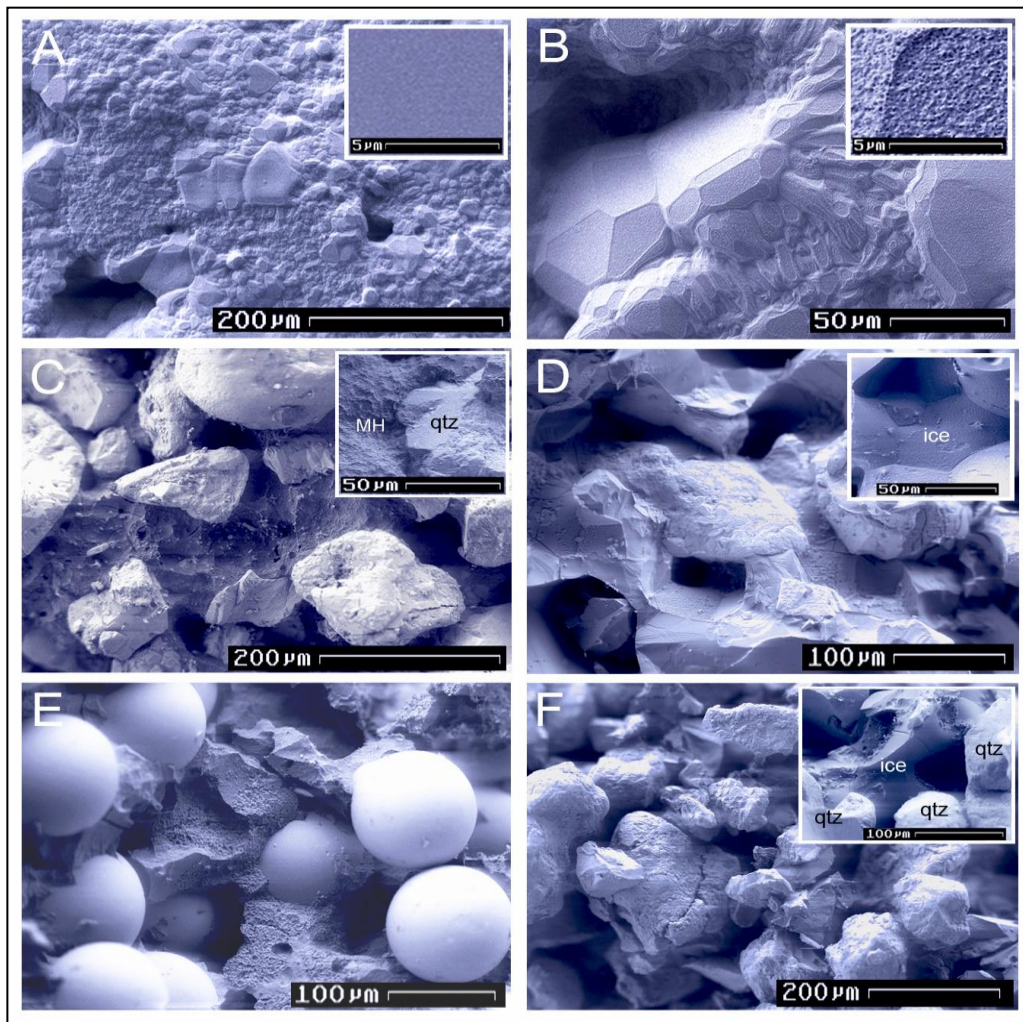
Hydrate was synthesized using a temperature cycling technique developed at USGS to fully-react  $\text{H}_2\text{O}$  ice and pressurized  $\text{CH}_4$  (15-30 MPa) into polycrystalline methane hydrate [Stern *et al.*, 2004]. We developed a pressure cell to synthesize  $\text{CH}_4$  hydrate while measuring *in situ* electrical conductivity (Figure 2). Starting samples comprised of granular ice that was free of sediment, mixed with quartz sand (OK#1), or mixed with silica glass beads. Mixtures were made in varying proportions with 100-10vol% ice and 0-90vol% sand or beads. Comparative measurements were performed on some samples after dissociation of hydrate to ice by venting  $\text{CH}_4$ .



**Figure 2.** Pressure vessel used to synthesize  $\text{CH}_4$  hydrate and measure conductivity.

### What do samples look like?

After full reaction to hydrate and subsequent testing, sample characteristics and phase distribution were assessed by cryogenic scanning electron microscopy (cryo-SEM) using the same techniques and instrumentation first described in *Fire in the Ice vol. 2 issue 2*.



**Figure 3.** Cryo-SEM images of hydrate-sediment mixtures. A and B show single-phase (unmixed), polycrystalline CH<sub>4</sub> hydrate with 20% porosity. Hydrate grains typically range 10-80 microns in diameter and are fully dense as-grown (A, inset) but developed surface pitting with time in the high-vacuum SEM column (B, inset). C shows a 50:50vol% hydrate:sand sample and D shows a 50:50vol% ice:sand sample. Significant annealing of the ice grains accompanies dissociation at our test conditions (compare D and C insets), but there was no significant migration of sand, thus enabling comparison of measurements before and after dissociation. E shows a 50:50vol% hydrate:beads sample. SEM shows uniform distribution of phases in all three samples (C, D, and E) as well as similarities in the nature of the grain contacts, helping establish a basis for comparison of conductivity measurements. F shows a 10:90vol% ice:sand sample, with some of the connecting ice expanded in the inset.



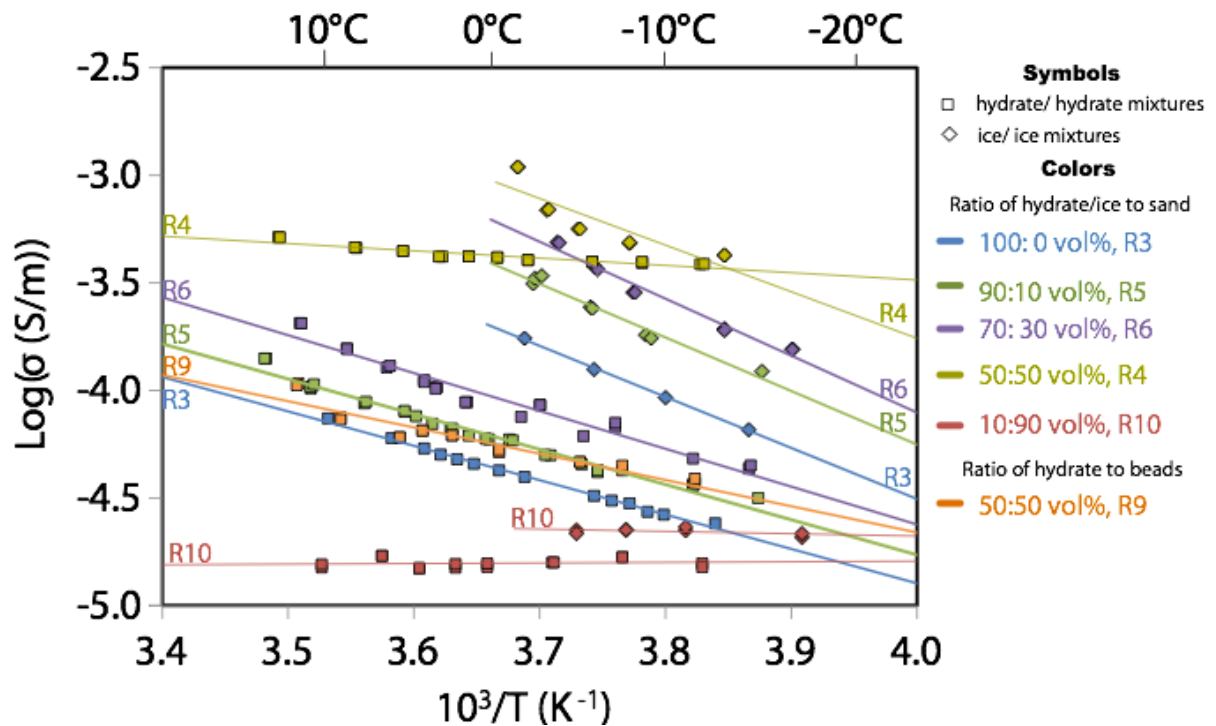
## Electrical conductivity

Impedance spectra (20 Hz to 2 MHz) were collected throughout each run and used to calculate conductivity. Conductivity had typical exponential dependence on temperature:

$$\sigma(T) = \sigma_0 * e^{-E_a/RT}$$

where  $\sigma_0$  is a pre-exponential constant,  $E_a$  is activation energy,  $R$  is the gas constant, and  $T$  is temperature. Plotting  $\log(\sigma)$  versus  $10^3/T(K)$  gives slopes that are proportional to  $E_a$  which characterizes the temperature dependence (Figure 4).

Conductivity measurements of unmixed  $\text{CH}_4$  hydrate (i.e. no sediment, shown in blue) ranged between  $10^{-5}$  to  $10^{-4}$  S/m. After the unmixed hydrate was dissociated, we measured conductivity of unmixed ice which was ~400% higher, with ~50% higher activation energy. The conductivity of  $\text{CH}_4$  hydrate is much less than seawater ( $\sim 10^{-1}$  to  $10^1$  S/m) and much greater than quartz ( $< 10^{-18}$  S/m).



**Figure 4.** Electrical conductivity measurements versus inverse temperature for various hydrate-sediment mixtures.

To evaluate the effects of sediments we measured the conductivity of  $\text{CH}_4$  hydrate mixed with either quartz sand (OK#1) or glass beads. We immediately noticed that hydrate samples containing sand had higher conductivity than samples without sediment, which is counterintuitive because the quartz sand by itself has very high resistivity. Increased sand concentrations, up to 50vol%, resulted in increased conductivity and decreased  $E_a$  (green, purple, yellow). Sand had similar affect on samples with dissociated ice. However the

sample with 10:90vol% hydrate:sand had much lower conductivity. Lower conductivity likely resulted from poorly connected hydrate, whereas sand connectivity had a smaller effect on conductivity. This indicates that the majority of electrical current conducts through the hydrate/ice and not the sand.

Fine particles on the weathered surfaces of the sand likely increased the concentrations of impurities and charge carriers in the surfaces of hydrate/ice grains, which lead to increased surface conductivity. To evaluate this mechanism further we measured a sample with 50:50vol% hydrate:beads (shown in orange). The synthetic glass beads are significantly less weathered and higher purity than the natural quartz sand, and hence we observed a less pronounced surface conductivity contribution.

## **Next Steps**

Our measurements have been successful in determining the electrical conductivity of single-phase methane hydrate and reveals general trends by comparison of various ice/sediment mixtures to hydrate/sediment mixtures. Such factors as chemical impurities, surface conductivity, sediment angularity, and porosity and permeability issues – just to name a few – still require greater investigation to fully understand their contributions and competing mechanisms. On a more fundamental materials science perspective we could also examine defect structure of CH<sub>4</sub> hydrate using different electrode materials. Other specific directions of interest for future work involve measuring CO<sub>2</sub> hydrate ( $\pm$ sediment), where CSEM may play a role in monitoring CO<sub>2</sub> sequestration in storage sites such as at Snøhvit.

## **Suggested reading:**

- Du Frane WL, LA Stern, KA Weitemeyer, S Constable, JC Pinkston, and JJ Roberts (2011), Electrical properties of polycrystalline methane hydrate, *Geophys. Res. Lett.*, 38, L09313. doi:10.1029/2011GL047243.
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- Stern LA, Kirby SH, Circone S, and Durham WB (2004). Scanning electron microscopy investigations of laboratory-grown gas clathrate hydrates formed from melting ice, and comparison to natural hydrates. *Am. Mineral.* 2004;89(8-9):1162-1175.
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- Weitemeyer KA, Constable S and Tréhu AM (2011). A marine electromagnetic survey to detect gas hydrate at Hydrate Ridge, Oregon, *Geophys. J. Int.*, doi: 10.1111/j.1365-246X.2011.05105.x.

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